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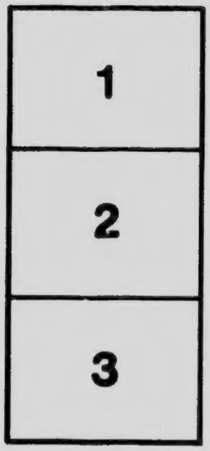

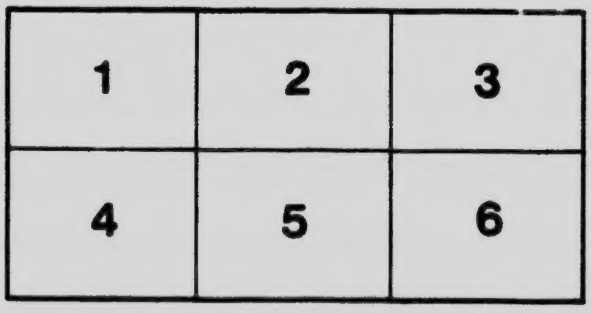

UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE PHYSICAL LABORATORIES

No. 55: ON THE IONISATION OF METALLIC VAPOURS IN FLAMES, BY PROFESSOR J. C. McLENNAN and DAVID A. KEYS

(REPRINTED FROM THE PROCEEDINGS OF THE ROYAL SOCIETY, A, VOL. 92.)

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On the Ionisation of Metallic Vapours in Flames.

By Prof. J. C. McLENNAN, F.R.S., and DAVID A. KEYS, M.A., University of Toronto.

(Received July 17, 1916.)

1. *Introduction.*

It has been shown by Frank and Hertz* and also later by McLennan and Henderson† that when electrons possessing kinetic energy corresponding to a fall of potential of approximately 4·9 volts are allowed to impinge upon heated mercury vapour in a vacuum, the vapour emits a monochromatic radiation of wave-length $\lambda = 2536{\cdot}72$ A.U. R. W. Wood‡ has also shown that if light of this wave-length be projected in a given direction into heated mercury vapour in a vacuum, the phenomenon of resonance comes into play and a radiation of wave-length $\lambda = 2536{\cdot}72$ A.U. is re-emitted by the vapour in directions making all angles with that of the impinging light. Quite recently too it has been shown by McLennan and Thomson§ that if mercury vapour be introduced into the flame of a Bunsen burner there issues from the flame in addition to the ordinary well-known light of the Bunsen flame the monochromatic radiation of wave-length $\lambda = 2536{\cdot}72$ A.U. These illustrations serve to show then that there are at least three distinct agencies by means of which the vapour of mercury may be brought into a state in which it is capable of emitting the characteristic monochromatic radiation of wave-length $\lambda = 2536{\cdot}72$ A.U. Frank and Hertz‖ have also shown—and it has later been confirmed by Newman¶—that mercury vapour is ionised when electrons are projected into it with a velocity equal to or greater than that acquired in a fall of potential of 4·9 volts. This result would therefore suggest that whenever mercury vapour is brought into a condition to emit the monochromatic radiation $\lambda = 2536{\cdot}72$ A.U., it is also ionised and should be capable of exhibiting electrical conductivity. Some experiments made by Steubing** also seem to support this suggestion, for he found that mercury vapour could be made conducting by simply passing through it light of wave-length $\lambda = 2536{\cdot}72$ A.U. It would seem, therefore, if this suggestion should urn out to be correct, that mercury vapour, when projected into a Bunsen flame, should become ionised and this ionisation should be made manifest by an increase in the ordinary conducting power of the flame. Though numerous investigators have experimented upon the electrical conductivity of salts of different metals in flames, but few appear to have made a study of the conductivity of the vapours of the simple metals themselves. Hittorf,* who investigated the conductivity of mercury vapour by heating the metal in a tube and passing the discharge from an induction coil through it, came to the conclusion that it was non-conducting. Herweg,† however, found that the vapour of mercury did conduct, but later still Braun‡ showed that mercury vapour when heated to 1000° C. did not exhibit any electrical conductivity.

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* Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 512 (1914).

† McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).

‡ R. W. Wood, 'Phys. Zeit.,' Jahrgang 10, No. 13, p. 425.

§ McLennan and Thomson, *supra*, p. 584.

‖ Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 10, pp. 457–467 (1914).

¶ Newman, 'Phil. Mag.,' vol. 28, pp. 753–756 (Nov., 1914).

** Steubing, 'Phys. Zeit.,' Jahrgang 10, No. 22, p. 787.

Sir J. J. Thomson,§ too, found that mercury vapour even at very high temperatures was a good insulator, a better one in fact than air, under similar conditions.

Strutt,‖ who investigated the electrical conductivity of mercury vapour in an evacuated quartz tube heated to redness, also found it to be an insulator.

E. N. da C. Andrade¶ has shown that strontium vapour increases the conductivity of a Bunsen flame and he has also presented some facts and conclusions drawn from them which lead to the view that the positively charged carriers in a flame containing a strontium salt are the metallic atoms of strontium. Pollok,** using pure vapours in a heated vacuum tube, found that the vapours of metals and their chlorides such as cadmium, zinc, and mercury conducted the current with great ease.

From the *résumé* just given it will be seen that no definite conclusions can be drawn regarding the state of ionisation of mercury in a Bunsen flame which is radiating monochromatic light of wave-length $\lambda = 2536{\cdot}72$ A.U. In view of certain theories of atomic structure which have been presented by Bohr†† and others, it is highly important to know whether mercury vapour which is in a condition to emit this radiation $\lambda = 2536{\cdot}72$ A.U. is ionised or not, and in order to obtain information on this point some experiments were made by the present writers and the results of these are given in the following communication.

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* Hittorf, 'Wied. Ann.,' vol. 7, p. 592 (1879).

† Herweg, 'Wied. Ann.,' vol. 9, p. 77 (1880).

‡ Braun, 'Zeit. f. Phys. Chem.,' vol. 13, p. 158 (1904).

§ J. J. Thomson, 'Phil. Mag.' (5), vol. 29, p. 384 (1890).

‖ Strutt, 'Phil. Mag.' (6), vol. 4, p. 326 (1902).

¶ E. N. da C. Andrade, 'Phil. Mag.' (6), vol. 139, p. 15 (1912), and 'Phil. Mag.' (6), vol. 138, p. 885 (1912).

** Pollok, 'Sci. Proc. Roy. Dublin Soc.,' N.S., vol. 13, p. 209 (1911–13).

†† Bohr, 'Phil. Mag.,' vol. 26, pp. 1, 476 and 857 (1913); vol. 27, p. 506 (1914); vol. 30, p. 394 (1915).

2. *Preliminary Experiments with Mercury.*

In making some preliminary experiments with mercury vapour a Bunsen burner A, fig. 1, was surrounded by a large earth-connected iron cylinder BB

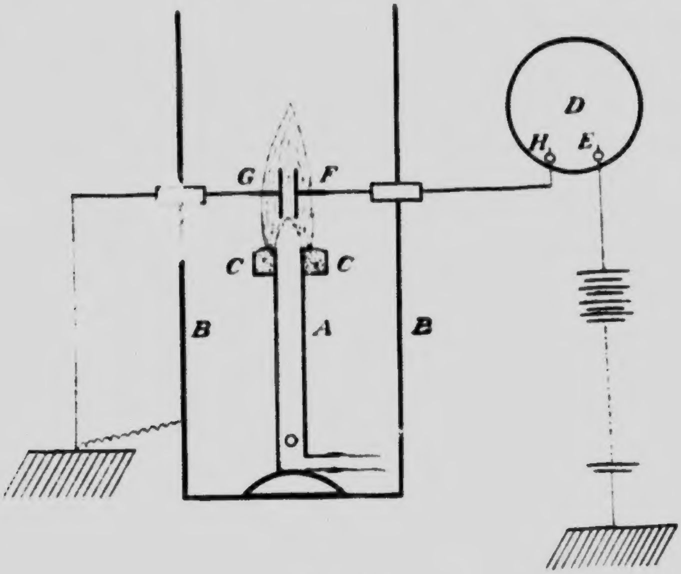

Fig. 1.

for the purpose of screening off air currents from the flame. The burner, which was provided at the top with a close fitting tubular steel cup CC, was also connected to earth. A sensitive D'Arsonval galvanometer, D, was placed upon an insulated stand and one of the terminals, E, was joined to one end of a battery of small storage cells, the other end of which was earthed. Two carefully cleaned platinum discs, F and G, carried by insulating supports were held in position in the flame. One of these, F, was joined to H, the second terminal of the galvanometer, and the other, G, was joined to earth. The discs F and G were each 3 cm. in diameter. With this arrangement it was found that, as soon as the Bunsen burner was lighted with the tubular cup, CC, empty, the galvanometer showed a deflection which indicated that a current was passing through it and that the flame was conducting. When the current was steady and a few drops of mercury were put into the cup, CC, an increase in the galvanometer deflection immediately took place. The heat from the flame warmed the cup and this was sufficient to vaporise the mercury and supply the flame with a stream of the vapour. This increase in the current was taken as showing directly that the vapour in the flame was ionised. In some additional experiments photographs were taken of the flame and it was always found when the cup, CC, was empty and free from mercury that the Bunsen flame spectrum alone was obtained. When, however, mercury was introduced into the cup and the increased conductivity was exhibited, the single spectral line $\lambda = 2536{\cdot}72$ A.U. always came out on the plates in addition to the flame spectrum. In no case was any trace of any other spectral line within the region between $\lambda = 6000$ A.U. and $\lambda = 1800$ A.U. obtained. It was thought that possibly the line $\lambda = 1849{\cdot}6$ A.U. might have come out on the plates, even though feebly marked, but it was never observed. In so far then as these experiments go the results indicate that the emission by the vapour of the monochromatic radiation of wave-length $\lambda = 2536{\cdot}72$ A.U. connotes ionisation of the vapour. The experiments also support the view that when the vapour acquires the power to emit the radiation, it simultaneously acquires the power to conduct electricity. Further, it follows, since for the stimulation of the mercury vapour to the emission of the radiation $\lambda = 2536{\cdot}72$ A.U. by electrons, it is necessary for the latter to have kinetic energy corresponding to a fall of potential of 4·9 volts, that the experiments described go to confirm the conclusion drawn by Frank and Hertz from direct experiment that 4·9 volts is the ionising potential of mercury vapour.

3. *Further Experiments with Mercury.*

With the apparatus used in the preliminary experiments it was found difficult to maintain the current through the flame steady for long periods of time, but after several trials the modification of the burner shown in fig. 2 was found to give very satisfactory results. To the top of an ordinary Bunsen burner a brass cylinder, KL, 3·8 cm. in diameter and 8 cm. in height, was soldered. The top was closed by a lid provided with an aperture 1·8 cm. in diameter, into which there was inserted a short tube 0·5 cm. in length. Another brass cylinder, 2·8 cm. in diameter and 7 cm., in length was held in the centre of the tube, KL, by means of three asbestos supports. This inner cylinder contained a fused quartz tube, F, 1 cm. in diameter and about 8 cm. in length, drawn off to a neck about 0·5 cm. in diameter at the upper end. A coil of manganin wire, MN, was wound round this quartz tube, and the ends were led out as shown in the figure through two openings in the cylinder, KL, fitted with small porcelain insulating plugs. A layer of asbestos paper was wound round the coil of manganin wire, and then the whole space between the quartz tube and the brass tube next to it was filled with plaster of Paris, which on solidifying kept everything rigid. The top of the quartz tube, F, came just level with the mouth of the burner. When the gas was lighted a large clear Bunsen flame was easily maintained above the mouth of the burner. The two electrodes, A and B, were placed in the centre of the flame as shown in the figure, and the connections with the galvanometer and the battery were the same as before. The burner and the screening iron cylinder, CD, were both kept well earthed. With this form of burner mercury could be inserted in the quartz tube, and before a heating current was passed through the circuit a set of readings could be taken on the conductivity of the simple flame. A steady current of sufficient intensity to bring the furnace up to a selected temperature could then be sent through the circuit, MN, and in this way a steady stream of mercury vapour could be supplied to the flame. The conductivity of the flame could then be investigated under these conditions and the proportion contributed by the vapour ascertained. With this form of burner it was found that exceedingly steady readings could be obtained, provided sufficient time was allowed to elapse after the heating current was turned on for the furnace to reach thermal equilibrium with its surroundings. As the burner as well as the electrode A was earthed, it will be seen that part of the current in the flame always went to each of them. This, however, made no difference, for the readings taken

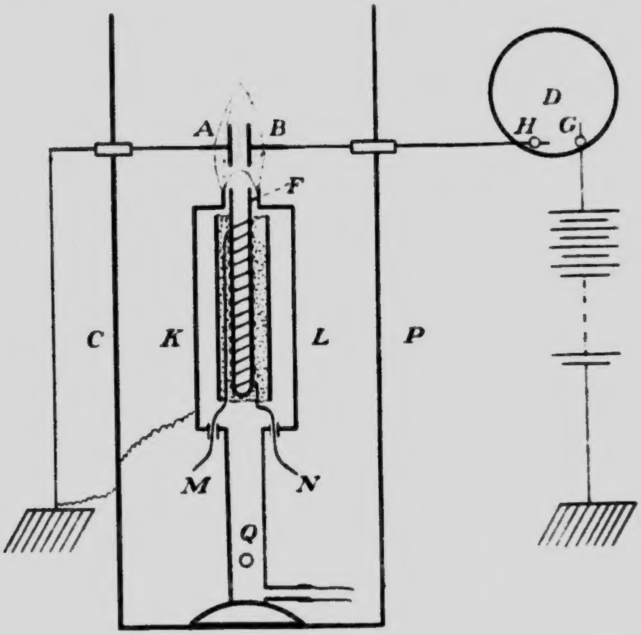

FIG. 2.

were always comparative ones, the one set being taken with the free flame and the other when it was kept supplied with the mercury vapour.

In a particular set of experiments, which will serve to illustrate the conductivity of the mercury vapour in the flame, a series of readings given by the galvanometer was taken when the potential of the battery was varied from 5 up to 237 volts, and the flame was free of mercury. A current of 5·5 ampères was then sent through the heating circuit, and when the furnace attained thermal equilibrium with its surroundings and the supply of mercury to the flame was steady, the second set of readings was taken with the same applied voltages. Table I gives the results of this particular experiment. The applied voltages are given in column I, and the galvanometer deflections without and with the mercury vapour are given in columns II and III respectively. The differences between these readings are given in column IV, and they represent the measures of the conductivity contributed by the vapour. Curves corresponding to the readings in columns II and III are given in fig. 3, and the curve in fig. 4 represents the differences given in column IV. From the form of the latter curve it will be seen that a saturation current was approximately obtained with the vapour when the applied potential was about 240 volts.

Table I.—Mercury.

Voltage.	Deflection without Hg.	Deflection with Hg.	Difference due to Hg.
Column I.	**Column II.**	**Column III.**	**Column IV.**
	cms.	cms.	cms.
5	1·3	2·4	1·1
20	2·4	4·2	2·8
40	3·4	6·5	3·1
60	4·8	8·8	4·0
80	5·2	10·2	5·0
95	5·9	12·2	6·3
112	6·4	13·2	6·8
132	7·2	13·8	6·6
157	7·6	14·4	6·8
177	8·0	16·8	8·8
197	8·6	17·2	8·6
217	9·0	18·0	9·0
237	9·8	20·4	10·6

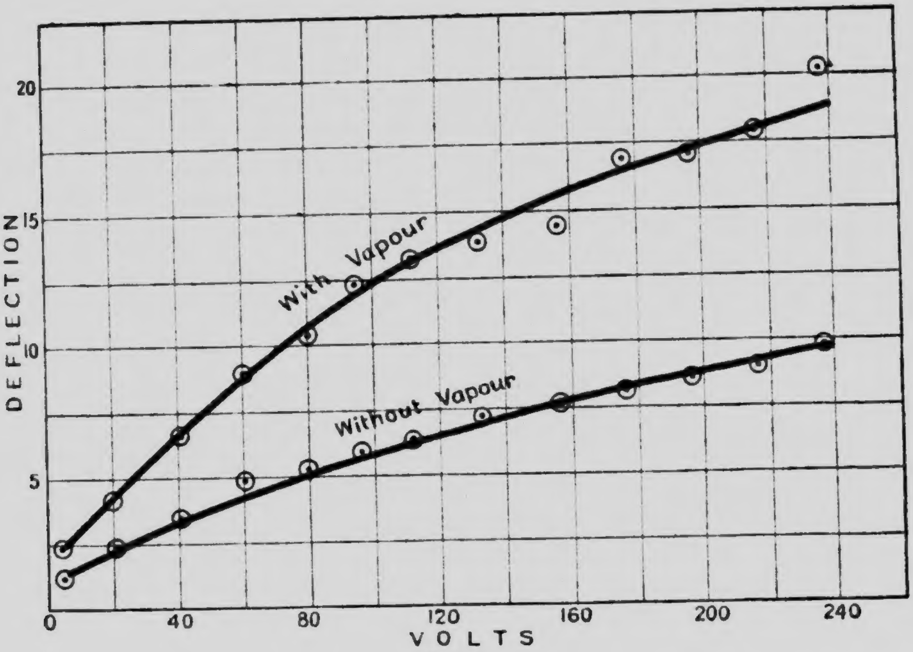

Fig. 3.

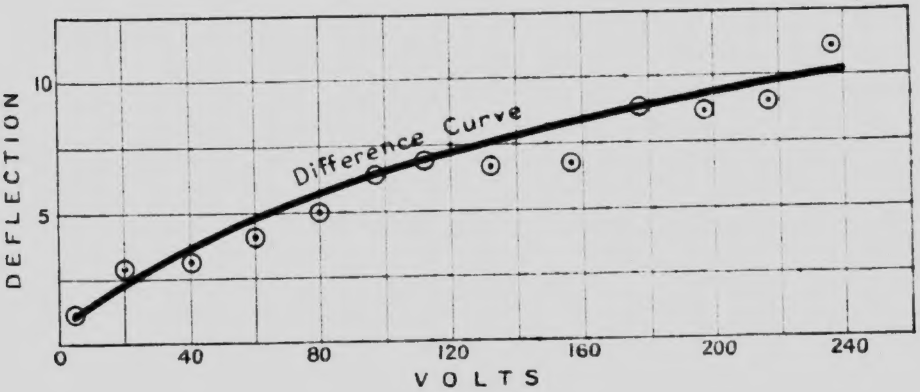

Fig. 4.

4. *Experiments with Zinc, Cadmium, Magnesium, and Thallium.*

Zinc.—In the paper on the flame spectra of metallic vapours by McLennan and Thomson*, it has been shown that, in their experiments on photographing the spectrum of a Bunsen flame into which a stream of zinc vapour was passed, no trace of any of the lines in the spectrum of zinc was obtained. Although the intensity of the flame was made as high as possible, nothing came out on the plates except the ordinary Bunsen flame spectrum. This result was rather surprising, for, in a previous paper by McLennan and Henderson,[*] it had been shown that it was possible to make zinc emit a spectrum consisting of the single line $\lambda = 3075{\cdot}99$ A.U., when the electrons were projected into the vapour with kinetic energy acquired in passing through a fall of potential of about 3·96 volts. Moreover, de Watteville[†] and also Ramage,[‡] found that, when sprays of solutions of zinc salts were sent into a Bunsen flame, this single line came out with great clearness. It would seem, therefore, that it is comparatively easy to stimulate the zinc vapour to the emission of light of this wave-length, especially when it is associated with a salt of this metal. In the experiments of McLennan and Thomson, however, as stated above, no trace of the line was obtained. It should also be pointed out that the lines $\lambda = 2536{\cdot}72$ A.U. and $\lambda = 3075{\cdot}99$ A.U. are respectively the first members of Paschen's[§] combination series $\nu = (2, p_2)-(m, \mathrm{S})$,[||] for the elements mercury and zinc, and that this was an additional reason for expecting that the zinc vapour in the flame would emit a radiation analogous to that emitted by the mercury vapour.

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* McLennan and Thomson, *supra*, p. 584.

In view of this result, it became interesting to see if zinc vapour, when led into a Bunsen flame, would produce any increase in the conductivity of the latter. The form of apparatus shown in fig. 2 was well suited to examine this point, for it was only necessary to insert a fresh quartz tube in the burner, and place pieces of the metal zinc in it instead of mercury. It was found quite easy to vaporise the zinc by means of the heating circuit, and on doing this it was found that the presence of the zinc vapour in the flame made no difference to the conductivity of the latter. A typical set of results is given in Table II. The applied voltages are given in column I, and the deflections without and with the vapour in the flame are given in columns II and III. The differences between the readings are given in column IV. These two sets of readings are plotted in fig. 5, and they show clearly that, for the range of temperatures investigated, the conductivity of the flame was quite unaffected by the presence of the zinc vapour in it. The experiments with zinc vapour, therefore, go to show that, if the zinc vapour is not subjected to a stimulation sufficiently intense to cause it to radiate light of a wave-length λ = 3075·99 A.U., it is not ionised.

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[*] McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).

[†] De Watteville, 'Phil. Trans. Roy. Soc.,' A, vol. 204, p. 139 (1904), and 'Comptes Rendus,' No. 142 (1906).

[‡] Ramage, 'Roy. Soc. Proc.,' vol. 70, p. 1 (1907).

[§] Paschen, 'Ann. der Phys.,' vol. 30, p. 746 (1909), and vol. 35, p. 860 (1911).

[||] In the symbolic equation $\nu = (n, \mathrm{X}) = (m, \mathrm{Y},)$ the frequencies are given by $\nu = \frac{\mathrm{N}}{[n+\mathrm{X}+x(n, \mathrm{X})]^2} - \frac{\mathrm{N}}{[m+\mathrm{Y}+y(m, \mathrm{Y})]^2}$, where N is Rydberg's number, n has a fixed value, either integral or one of the numbers 1·5, 2·5, 3·5, etc., and m has successive integral values, each one giving the frequency of a member of the series.

Table II.—Zinc. Distance between Plates 0·8 cm.

Volts. Column I.	Without zinc vapour. Column II.	With zinc vapour. Column III.	Difference. Column IV.
	cms.	cms.	cms.
6	1·6	1·5	−0·1
20	4·9	4·3	−0·6
40	6·9	7·4	0·5
60	9·2	10·2	1·0
78	11·9	13·0	1·1
102	15·6	15·3	−0·3
120	15·7	16·4	0·7
140	19·2	18·8	−0·4
161	19·6	20·4	0·8
181	21·4	25·2	3·8
201	22·1	23·0	0·9
221	31·0	29·1	−1·9
239	25·2	30·6	5·4

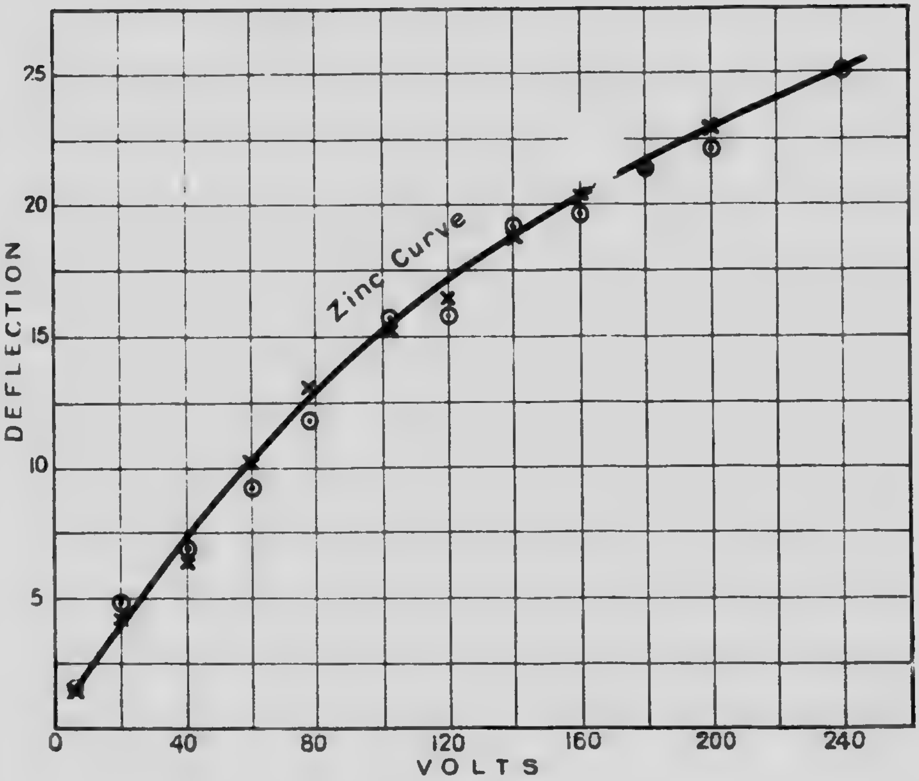

FIG. 5.

Cadmium.—In the spectrum of cadmium the lines $\lambda = 3260{\cdot}17$ Å.U. and $\lambda = 2288{\cdot}72$ Å.U. are specially important. They are respectively the first members of the combination series $\nu = (2, p_2)-(m, \mathrm{S})$, and of the singlet series $\nu = (1{\cdot}5, \mathrm{S})-(m, \mathrm{P})$. Moreover they are the only lines which are absorbed by non-luminous cadmium vapour in the region between $\lambda = 6000$ A.U. and $\lambda = 1900$ A.U. Further, according to de Watteville (*loc. cit.*) and Ramage (*loc. cit.*) the line $\lambda = 3260{\cdot}17$ A.U. is the only one which comes out in spectrograms of Bunsen flames fed with a spray of aqueous solutions of cadmium salts. If electrons be projected into heated cadmium vapour in a vacuum tube with kinetic energy equal to that acquired in a fall of potential of about 3·74 volts, it is found that the vapour radiates light of the wave-length $\lambda = 3260{\cdot}17$ A.U., and of this wave-length only. Further, it has been shown by McLennan and Thomson (*loc. cit.*), when using a burner similar to that shown in fig. 2, that if a stream of cadmium vapour be sent into the flame the line $\lambda = 3260{\cdot}17$ A.U. comes out quite strongly when the flame is burning, even with moderate intensity, and when the draught is forced and a larger supply of the gas provided, so that the flame burns strongly, the line $\lambda = 2288{\cdot}72$ A.U. comes out as well as the line $\lambda = 3260{\cdot}17$ A.U. However, when experiments were made by the writers, both with strong and with moderate flames, the conductivity was the same when the flame was supplied with cadmium vapour as when none of the vapour was present. Contrary then to what was expected these experiments lend no support to the view that cadmium vapour is ionised when it is in a state which renders it capable of radiating light of wave-length $\lambda = 3260{\cdot}17$ A.U. or even of radiating light of wave-length $\lambda = 2288{\cdot}72$ A.U.

Magnesium.—In the spectrum of magnesium the line $\lambda = 2852{\cdot}22$ Å.U. appears to be the one of special importance. It is the first line, according to Lorenser;* of the singlet series $\nu = (1{\cdot}5, \mathrm{S})-(m, \mathrm{P})$. It and also the line $\lambda = 2026{\cdot}46$ A.U. have been shown by one of us† to be strongly absorbed by non-luminous magnesium vapour. It has also been shown by one of us (*loc. cit.*) to be the only line in the magnesium spectrum emitted by the vapour of this metal under bombardment by electrons with kinetic energy acquired in a fall of potential of from 4 to 5 volts. Moreover, as de Watteville (*loc. cit.*) and Ramage (*loc. cit.*) have shown, it is the only line of the magnesium spectrum which comes out in the spectrum of a Bunsen flame fed with the spray of aqueous solutions of magnesium salts.

Liveing and Dewar‡ observed the line $\lambda = 4571{\cdot}38$ Å.U. in the spectrum of the light from magnesium burning in air, and Eder and Valenta* also found it in the spectrum of the light from a Bunsen flame fed with magnesium powder. Both of these pairs of investigators, however, found other magnesium lines as well in their spectrograms, and the evidence which their work offers, while emphasising the importance of the magnesium line $\lambda = 4571{\cdot}38$ A.U. in the magnesium spectrum, does not definitely point to its having altogether a fundamental character. The evidence rather goes to show that it is possible to stimulate magnesium vapour to the emission of light of wave-length $\lambda = 2852{\cdot}22$ A.U. without an accompanying emission of light of wave-length $\lambda = 4571{\cdot}38$ A.U., and that when the stimulation results in the appearance of $\lambda = 4571{\cdot}38$ A.U. in the spectrum, it is necessarily accompanied by the line $\lambda = 2852{\cdot}22$ A.U. It is the line $\lambda = 2852{\cdot}22$ A.U. which appears to be the fundamental one. In view of the importance of this line in the spectrum of magnesium, it is of considerable interest to know whether or not magnesium vapour when it is in a state to emit the radiation is also in a state to exhibit electrical conductivity. Our experiments, therefore, were extended to include a study of the conductivity of flames fed with the vapour of this metal. The apparatus again used was that shown in fig. 2. In this case it was found that the conductivity of the Bunsen flame was greatly increased as soon as the magnesium vapour was sent into it. It was also shown that simultaneously with the occurrence of the increased conductivity the vapour in the flame began to emit strongly the monochromatic radiation of wave-length $\lambda = 2852{\cdot}22$ A.U. The results of one of a number of sets of observations are recorded in Table III. The applied voltages are given in column I, and in column II the galvanometer deflections before the vapour was sent into the flame. In column III the deflections are recorded which were obtained when the furnace had reached thermal equilibrium and the flame was being fed with a steady stream of vapour. Column IV contains a set of deflections obtained a few hours after the heating circuit had been cut off and the furnace had become cooled down to room temperature. Column V contains the differences between the readings in columns III and IV. Curves representing these deflections are shown in fig. 6. It will be noted from the deflections in columns II and IV that the conductivity of the flame was much less before any magnesium vapour had been sent into it than what it was after the furnace had been cooled down and the supply of vapour cut off. The explanation of this high residual conductivity of the flame caused some trouble at first but it was finally traced to the existence of a fine layer of magnesium oxide which had become deposited upon the electrodes while the

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* Lorenser, 'Inaug. Diss.,' Tübingen (1913).

† McLennan, *supra*, p. 574.

‡ Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 32, p. 189 (1881).

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* Eder and Valenta, 'Atlas Typischer Spektren,' p. 18.

Table III.—Magnesium. Distance between Electrodes = 0·85 cm.

Volts. Column I.	Without vapour. Column II.	With vapour. Column III.	Without vapour. Column IV.	Difference. Column V.
	cms.	cms.	cms.	cms.
6	1·0	42·5	14·9	27·6
20	1·9	148·8	39·7	109·1
38	2·9	255·0	67·0	188·0
58	3·9	357·0	96·7	260·3
77	4·9	425·0	121·5	303·5
101	5·5	505·8	136·4	369·4
118	6·3	552·5	156·2	396·3
138	7·1	629·0	191·0	438·0
152	7·6	663·0	198·4	464·6
172	8·4	722·5	208·3	511·2
190	8·8	726·8	218·2	508·6
210	9·2	748·0	231·8	516·2
229	9·8	773·5	243·0	530·5

flame was being fed with the vapour. The differences between the readings in columns III and IV, namely, the numbers in column V, may be taken, therefore, to represent the conductivity actually contributed by the vapour in the flame under steady conditions. It is of interest to note that with magnesium as with mercury saturation was obtained with about 240 volts. With magnesium it would appear then that when the vapour in the flame is in the condition to emit monochromatic radiation of wave-length $\lambda = 2852{\cdot}22$ A.U. it is also strongly ionised. One cannot say definitely, however, that the conditions which determine the ionisation are the same as those which give the vapour the power to emit the radiation $\lambda = 2852{\cdot}22$ A.U. alone. We have seen that with cadmium vapour in the Bunsen flame it was possible to obtain the line $\lambda = 3260{\cdot}17$ A.U. and the line $\lambda = 2288{\cdot}72$ A.U. The line $\lambda = 2852{\cdot}22$ A.U. has been shown recently by Lorenser* to be the first line of the singlet series $\nu = (1{\cdot}5, S) - (m, P)$, and the line $\nu = 2026{\cdot}46$ A.U. the second member of this series. As pointed out above both of these lines characterise the absorption spectrum of magnesium vapour and it is possible that radiations corresponding to both of them and to other members of the series as well were emitted by the vapour-laden flame but that the intensity of the radiation of the members of the higher frequencies was too weak to leave any impression on the photographic plates. All that can be said definitely is that the vapour in the flame was ionised and that at the same time it was strongly emitting monochromatic light of wave-length $\lambda = 2852{\cdot}22$ A.U. As indicated above the line in the magnesium spectrum given by $\nu = 2$, $p_2 - 1{\cdot}5$, S, and corresponding to the lines $\lambda = 2536{\cdot}72$ A.U., $\lambda = 3076{\cdot}99$ A.U. and $\lambda = 3260{\cdot}17$ A.U. in the spectra of mercury, zinc, and

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* Lorenser, 'Inaug. Diss.,' Tübingen (1913).

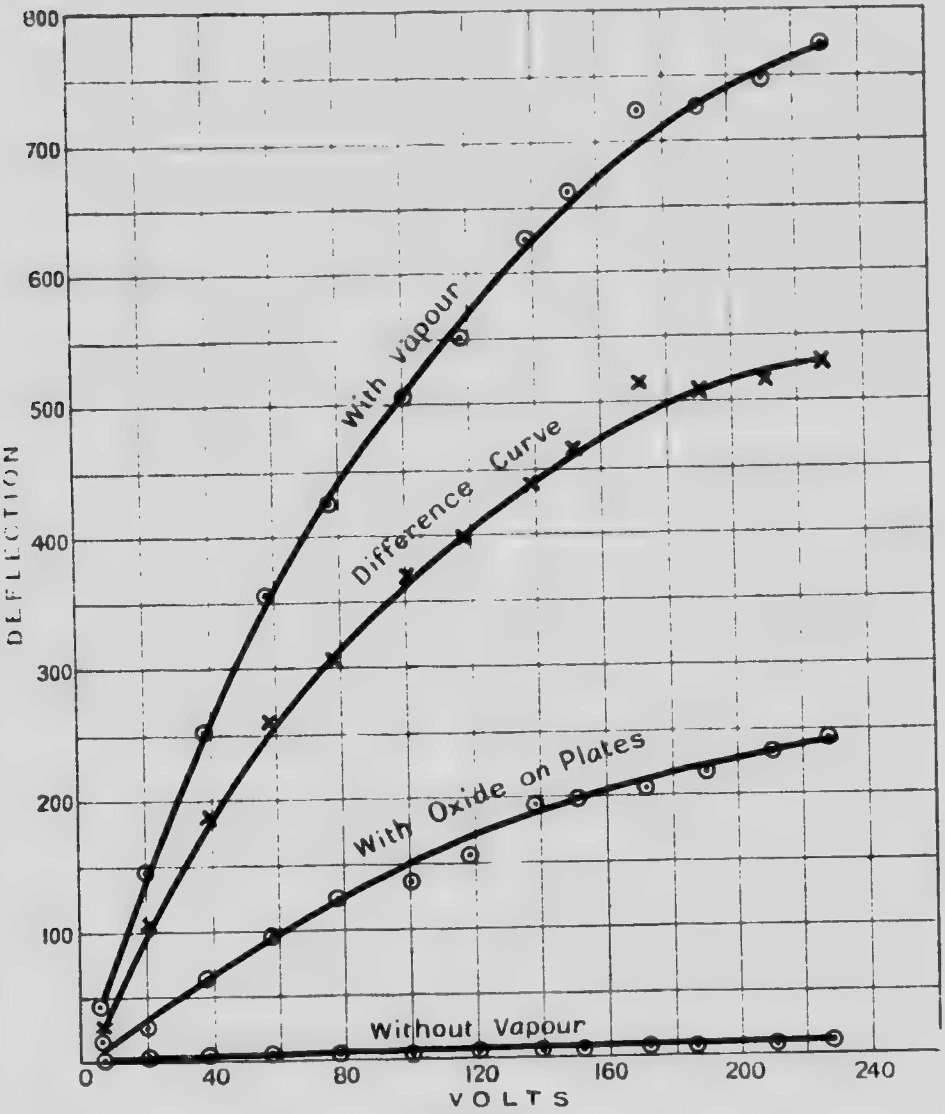

Fig. 6.

cadmium respectively is given by $\lambda = 4571{\cdot}38$ A.U. This line has been found in the arc spectrum of magnesium, and as already mentioned it has been found by some experimenters in the Bunsen flame spectrum of magnesium, but in none of the experiments made by us with the magnesium vapour-laden flames was any trace of the line obtained in the spectrograms taken. Moreover, in some experiments made by one of us* some time ago and recently repeated it was found that when electrons were projected into magnesium vapour in a vacuum with gradually increasing velocities no trace of a spectral line was obtained in the light from the vapour until the electrons were given a speed corresponding to between 4 volts and 5 volts fall of potential. When this speed was reached $\lambda = 2852{\cdot}22$ A.U. came out strongly on the plates. With still greater speeds no additional lines came out until the kinetic energy of the electrons corresponded to a fall of potential of about 7·5 volts. When this potential was reached the arc suddenly struck and the many-lined spectrum came out. Combining all these results it would seem that in the case of magnesium vapour, ionisation does not take place until the conditions are such as to enable the vapour to radiate light of wave-length $\lambda = 2852{\cdot}22$ A.U. If this be so it would appear that on the quantum theory the frequency of the line $\lambda = 2852{\cdot}22$ A.U. is the one which determines the ionising potential of magnesium vapour. From the equation $Ve = h\nu$ it would appear then that the ionising potential for atoms of this metal is 4·28 volts.

Thallium.—Some experiments were also made on the conductivity of thallium vapour-fed Bunsen flames. With this metal it was found that the presence of the vapour greatly increased the conductivity of the flame and that it was difficult to obtain a saturation current. Table IV contains a set of readings taken with this metal and the curves in fig. 7 and 8 represent

Table IV.—Thallium. Distance between Electrodes = 0·9 cm.

Volts.	Without thallium vapour.	With thallium vapour.	Difference.
Column I.	Column II.	Column III.	Column IV.
	cms.	cms.	cms.
6	0·3	2·0	1·7
20	0·5	2·7	2·2
30	0·9	3·6	2·7
59	1·1	4·4	3·3
80	1·3	6·2	4·9
102	1·45	6·8	5·3
120	1·5	8·0	6·5
140	1·6	9·4	7·8
161	1·8	11·9	10·1
164	2·0	13·0	11·0
202	2·05	17·2	15·1
222	2·2	24·4	22·2
243	2·35	31·6	29·2

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* McLennan, 'Roy. Soc. Proc.,' A, vol. 92, p. 305 (1915).

them. In taking these readings the sensitiveness of the galvanometer was greatly reduced. At the same time as the readings were taken the spectrum of the flame was photographed and it was found that when the vapour was present in the flame the only lines in the spectrum of thallium which came out were those of wave-length $\lambda = 5350{\cdot}65$ A.U. and $\lambda = 3775{\cdot}87$ A.U. These lines are the first members of the second subordinate $\nu = (2.\ p_1)-(m,\ s)$,

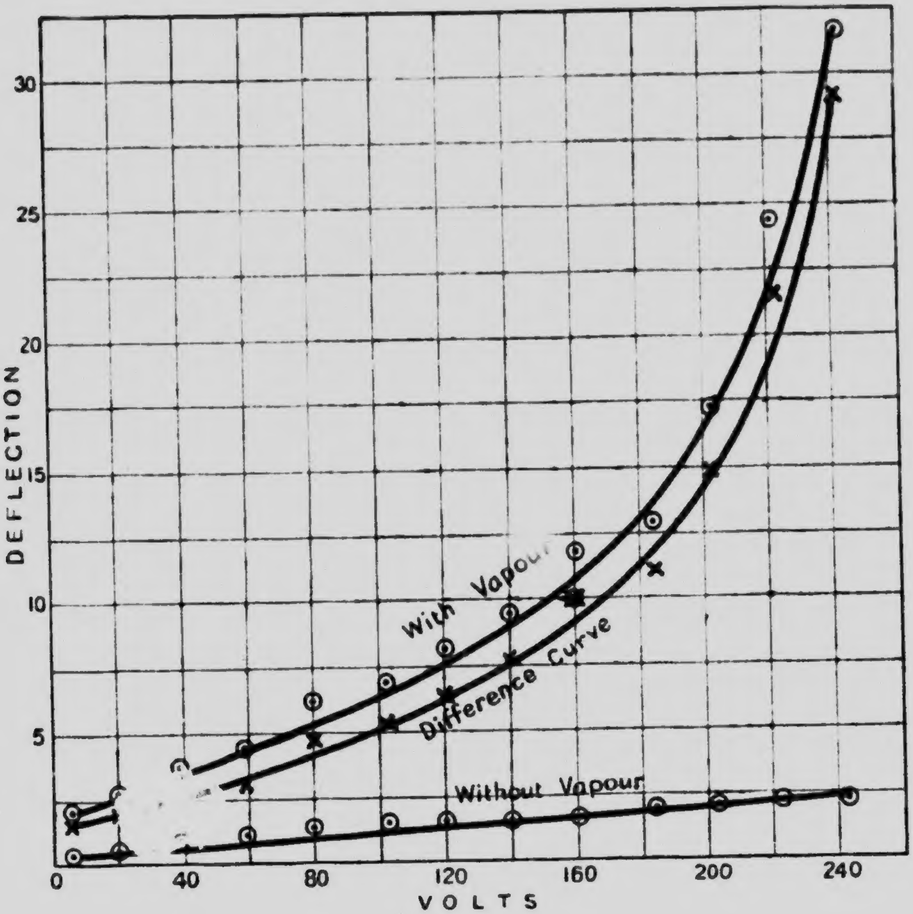

FIG. 7.

and $\nu = (2,\ p_2)-(m,\ s)$. The lines whose frequencies are given by $\nu = (1{\cdot}5, S)-(2, p_2)$, and $\nu = (1{\cdot}5, S)-(2, P)$, are not yet known for the spectrum of thallium, and consequently one cannot be certain where to look for them. They are probably, however, in the extreme ultra-violet region. Had they been known or been found one might have deduced the ionising potential for thallium vapour provided it were shown to act in a vacuum in a manner analogous either to the vapour of mercury, zinc, and cadmium or to that of magnesium. With thallium then the results show that the vapour of the metal increases the conductivity of a Bunsen flame, and that at the same time as the added conductivity is contributed radiations of the wave-lengths $\lambda = 5350{\cdot}65$ A.U. and $\lambda = 3775{\cdot}87$ A.U. are emitted. It should be pointed out in this connection that Ramage,* who investigated the spectrum of Bunsen flames into which metallic thallium or a spray of the aqueous solutions of thallium salts was injected, found the line $\lambda = 5350{\cdot}65$ A.U. to be the only one which came out in addition to the spectrum of the free flame.

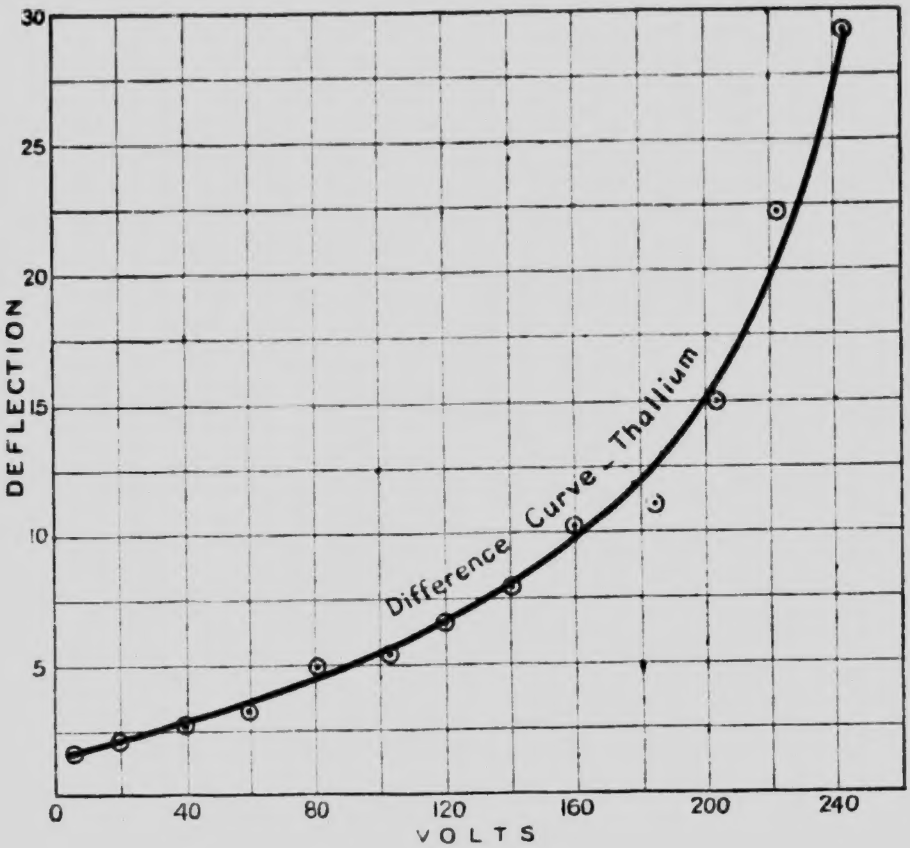

Fig. 8.

5. *Atomic Structure.*

It was expected in undertaking these experiments to arrive at some definite information regarding the nature of the atomic structure of the metals investigated. The results, however, are not conclusive. According to the theory advanced by Bohr,* ionisation of an atom can only be said to take place when the disturbing agency causes one or more of the electrons in an atom to be projected out from the permanent electronic system beyond [illegible] outermost stationary or non-radiating orbit of the atom. Su[illegible]ed electrons in returning to the permanent configuration could emit light of only one wave-length then if the atom possessed but at most one stationary or non-radiating orbit outside the permanent ones. The theory of Bohr, however, hypothecates many of these stationary orbits even for atoms of the simplest structure. It would follow then on this theory that if an atom emits light of but one wave-length it cannot be said to be ionised. The results of the experiments with mercury vapour would indicate that the theory is invalid, for the evidence goes to show that the radiation emitted by the atoms of the vapour was entirely monochromatic, and at the same time it supports the view that under these circumstance the vapour was ionised. The results with zinc are inconclusive. With cadmium, on the other hand, we find that the vapour in the flame emitted light of at least two wave-lengths, and yet the vapour did not appear to be ionised. This result supports Bohr's conception of atomic structure. The results obtained with magnesium vapour, just as those obtained with mercury vapour, are opposed to Bohr's theory, for with this vapour in the flame we obtained ionisation of the vapour and at the same time an emission of radiation of apparently but one wave-length. Finally, the results obtained with thallium vapour neither conclusively support nor definitely tend to invalidate the theory. While the radiation emitted by this vapour in the flame, as observed by us, consisted of light of but two wave-lengths, the collateral evidence available does not altogether support the view that the radiation actually emitted under the circumstances was really confined to light of these wave-lengths. It is possible and likely that radiation also took place in the spectral region beyond that which could be detected by a quartz spectrograph, which was the optical instrument used in this investigation. The fact that ionisation of thallium vapour in the flame was observed cannot therefore conclusively be used for or against Bohr's theory.

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* Ramage, 'Roy. Soc. Proc.,' vol. 70, No. 459, p. 1 (1902).

6. *Summary of Results.*

1. Mercury vapour which is fed into the flame of a Bunsen burner is ionised, and the radiation from the vapour consists of light of wave-length $\lambda = 2536 \cdot 72$ A.U.

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* Bohr, 'Phil. Mag.,' vol. 26, pp. 1, 476, 857 (1913); vol. 27, p. 506 (1914); vol. 30, p. 394 (1915).

2. Zinc vapour, when injected into Bunsen flames, is not ionised, and does not emit any light characteristic of the spectrum of zinc.

3. A Bunsen flame which is supplied with cadmium vapour emits light of wave-length $\lambda = 3260 \cdot 17$ A.U. when the intensity of the flame is weak, and when burning strongly it emits light of wave-length $\lambda = 2288 \cdot 79$ A.U. as well. The cadmium vapour in such flames does not appear to be ionised.

4. Magnesium vapour which is fed into the flame of a Bunsen burner emits light of wave-length $\lambda = 2852 \cdot 22$ A.U., and the vapour in the flame is ionised. The ionising potential for atoms of magnesium vapour appears to be 4·28 volts.

5. Thallium vapour, when it is fed into a Bunsen flame, becomes strongly ionised, and under these circumstances emits light of the wave-lengths $\lambda = 5350 \cdot 65$ A.U. and $\lambda = 3775 \cdot 87$ A.U.

6. The combined results of the investigation neither conclusively support nor definitely tend to invalidate Bohr's theory of atomic structure.

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